



ARTICLE

On the Theory of the Electrolytical Double Layer

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List of Symbols

c	molar concentration, also molarity, defined as the amount of a constituent n_i (in moles) divided by the volume of the mixture V , mol cm^{-3} or mol L^{-1}
C	concentration in mole fraction, dimensionless unit
C, C_0	Differential capacitance, $\frac{d\sigma}{d\varphi}$, F m^{-2} or $\text{A}^2 \text{s}^4 \text{kg}^{-1} \text{m}^{-4}$
e	elementary charge, $1.602\,176\,634 \times 10^{-19} \text{ C}$ or $4.806\,530 \times 10^{-10} \text{ e.s.u.}$ ($1 \text{ C} = 1 \text{ A s}$), $\mathcal{F} = e \cdot N_A$
$\mathcal{E}^+, \mathcal{E}^-$	Adsorption potential per mole, J mol^{-1}
\mathcal{F}	FARADAY constant, $9.648\,533 \times 10^4 \text{ C mol}^{-1}$ or $2.8946 \times 10^{14} \text{ e.s.u. mol}^{-1}$
k_B	BOLTZMANN constant, $1.380\,649 \text{ J K}^{-1}$
\mathcal{M}	molar mass, g mol^{-1}
n_1, n_2	number of adsorbed or dissolved molecules at equilibrium per 1 cm^2 and per 1 cm^3 , respectively
$\mathbf{n}_1, \mathbf{n}_2$	number of maximum molecules, either adsorbed or dissolved, per 1 cm^2 and per 1 cm^3 , respectively
N_A	AVOGADRO constant, $6.022\,140 \text{ mol}^{-1}$
Q	Adsorption heat per mole of salt, J mol^{-1}
\mathcal{R}	universal gas constant, equals $k_B \cdot N_A$, $8.314\,462 \text{ J mol}^{-1} \text{ K}^{-1}$
t_1, t_2	time interval, at which one molecule is located at the boundary surface and in the solution, respectively
T	Temperature, K
W	Work, J or $\text{kg m}^2 \text{s}^{-2}$
x, y, z	cartesian coordinates, x, y span the plane corresponding to the metal-solution-interface, z points in the direction of the solvent/solution
z^+, z^-	number of positive and negative charged ions adsorbed on the boundary surface, cm^{-2}
Z	number of moles per ion

δ	medium distance between the ion centers, equals approximately the ionic radius
ε_0	vacuum permittivity, electric constant, $8.854\,187 \times 10^{-12} \text{ F m}^{-1}$
$\tilde{\varepsilon}_r$	relative permittivity of the ions, dimensionless
ε_r	dielectric constant or relative permittivity of the solvent or of water (80 at 20 °C), dimensionless
ζ	Zeta potential, electrokinetic potential, V or mV
$\rho(z)$	density of positive charge, V m^{-2}
ϱ	density, kg m^{-3}
σ	surface charge density (amount of electric charge per unit surface area) on the metal surface or in the electrolyte per electrode surface area, C m^{-2}
φ	electric potential, electric surface potential, V or $\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$
φ_0	total thermodynamic potential difference between the interior of the solution and the interior of the metal
φ_1	potential difference in a plane parallel to the metal/solution interface at a distance δ
$\overline{\varphi}_0$	total potential difference in the diffuse layer
ϵ^+, ϵ^-	specific adsorption potential, J
$1, 2$	first and second molecular layer

Introduction

If one immerses an Ag sheet in a 0.1 N AgNO_3 solution, the sheet becomes positively charged compared to the solution. According to NERNST, this happens because silver ions from the solution precipitate on the sheet and charge it positively and, upon reversion, the solution negatively until the resulting electrostatic forces prevent the sheet from being further charged. The positive charges of the silver are located on the surface of the sheet, the negative charges (NO_3^-) of the solution are also located on its surface. An electrical double layer is created at the sheet metal-solution interface. The sheet and the solution are conductors; the electrical potential inside them is constant; the entire potential difference between the sheet and the solution is to be found in the double layer at the interface. The same applies to every interface of an electrolyte solution. We refer to the electrical double layer at such an interface as “*electrolytic double layer*”.

The questions arise:

1. How much Ag^+ are precipitated until the equilibrium is reached, i.e. what is the value of the charge in the double layer? If we are able to answer this question, we have the theory of polarization capacitance and the electrocapillary curve.
2. What is the structure of the double layer, in particular how far does it extend into the solution? The answer to this question will allow us to develop a theory of electrokinetic phenomena (Endosmosis¹, cataphoresis, etc.²).

To answer both questions, it makes a significant difference whether one considers the forces acting on the ions only as those resulting from their charges and the potential difference, or whether special interface forces, i.e. the specific adsorption of the ions at the interface, are taken into account. In the following, under section 1 and section 2 the two previously established theories, without taking adsorption into account, under section 3 to section 5 the new theory, without and with adsorption should be discussed³. For the sake of simplicity, only the case of a flat and smooth interface and a monovalent electrolyte is taken as a basis; generalization to the case of any number of ion types of any valence presents no difficulties. In order to be able to express ourselves more briefly, we will always consider the metal as positively charged and the solution as negatively charged, but of course all considerations apply exactly the same to the opposite case.

1. The Theory of the Molecular Capacitor

The simplest theory, which follows the original HELMHOLTZ theory, is that the entire charge of the solution lies in the form of an excess of negative ions in the molecular layer directly adjacent to the metal surface. In the case considered above, $\text{Ag}/0.1\text{ N AgNO}_3$ ⁴, the excess of NO_3^- equivalent to the precipitated Ag^+ remaining in the solution would be directly located on the metal surface. This double layer is then idealized and replaced by a plate capacitor by blurring the discrete charges on the individual ions to form a homogeneous surface charge distribution, the positive coating of which forms the surface of the silver, while the negative coating is located in the solution on a plane parallel to the former at a distance δ . Here δ is

¹Endosmosis occurs between two liquids of different chemical composition separated by a porous membrane.

²Cataphoresis, also called electrophoresis, stems from the word cathode, which means that positively charged particles are moving towards a cathode, see <https://en.wikipedia.org/wiki/Electrophoresis>

³The reason for this work were the fundamental publications of DEBYE on the theory of electrolytes.

⁴a 0.1 N AgNO_3 corresponds to a 0.1 mol L^{-1} silver nitrate solution.

the average distance of the ion centers, or to be more precise, the electrical centers of gravity of the ions from the metal surface; δ is approximately equal to the ionic radius. In the following we will assume that δ is the same for the positive and negative ions, i.e. we shall calculate with a median ionic radius. Furthermore, if $\tilde{\varepsilon}_r$ is the dielectric constant (relative permittivity) of the medium located between the occupancies of the capacitor ($\tilde{\varepsilon}_r$ is therefore approximately equal to the dielectric constant of the ions⁵), φ_0 the electrical surface potential, i.e. the total potential difference between the interior of the solution and the interior of the metal and σ_0 is the charge per unit area (electrical surface charge density) or the electric charge in the diffuse layer, then the following equation applies according to the well-known formula for the capacity of a plate capacitor:

$$\sigma_0 = \frac{\tilde{\varepsilon}_r \varepsilon_0}{4\pi\delta} \cdot \varphi_0. \quad (1a)$$

with

$$\frac{d\sigma_0}{d\varphi_0} = C = \frac{\tilde{\varepsilon}_r \varepsilon_0}{4\pi\delta}$$

as the differential capacitance, which, in physics, electronics, and electrochemistry is a measure of the voltage-dependent capacitance of a nonlinear capacitor, such as an electrolytic double layer. The direct measurements of σ_0 on mercury electrodes using the electrocapillary curve result in an empirical capacity C per cm^2

$$C = \frac{\tilde{\varepsilon}_r \varepsilon_0}{4\pi\delta}$$

of the double layer capacitor of approximately $24 \mu\text{F}$. This results in a quotient $\frac{\delta}{\tilde{\varepsilon}_r \varepsilon_0} \sim 0.332 \times 10^{-8} \text{ cm}$ or 0.33 \AA , respectively, a quite plausible value. Figure 1 shows the potential curve and the charge distribution in the double layer. Here and in the following figures, the hatched area means the metal, the unshaded area means the solution. The abscissa is the distance from the metal/solution interface, the ordinate is the electrical potential φ .

⁵The following applies: $\varepsilon = \tilde{\varepsilon}_r \cdot \varepsilon_0$, with ε_0 as the dielectric constant and ε as the permittivity.

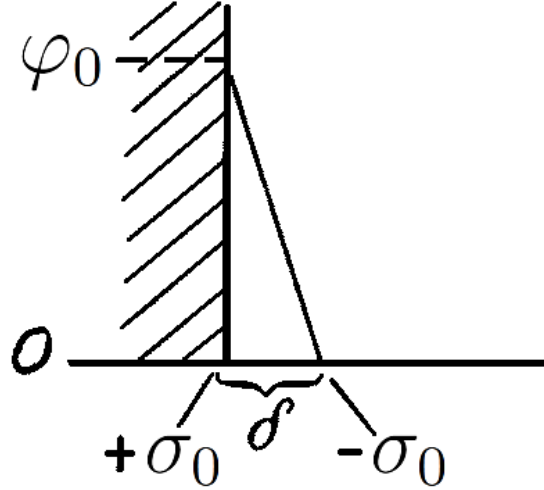


Figure 1: Curve progression of electrical surface potential and charge distribution dependent on δ at a metal (left)/solution (right) interface

2. The Theory of the Diffuse Double Layer

This theory, developed by GOUY and CHAPMAN, [1, 3, 4, 5], is based on the idea that the distribution of ions in the solution near the metal surface is determined by two opposing influences. While the movement due to molecular heat always strives to distribute the ions evenly, in such a way that on average there are an equal number of positive and negative ions in each volume element of the solution, the electrostatic forces emanating from the metal surface –again assumed to be positively charged– which implies attraction of negative ions, repulsion of positive ions, cause the volume elements located near the interface to contain an excess of negative ions. The equilibrium that is established under the influence of this counteraction of thermal motion and electrical forces will be quite analogous to the atmospheric equilibrium that is established in a gas under the influence of gravity. The excess of negative ions will be greatest immediately on the metal surface (on the ground!) and will decrease towards the inside of the solution according to a law corresponding to the barometric formula. GOUY and CHAPMAN obtain this law by determining the concentration of positive and negative ions at each point in the solution from the electrical potential φ prevailing there using an e Ansatz of BOLTZMANN and to calculate φ replacing the discrete charges on the individual ions with a continuous, spatial charge distribution. The density of negative electricity at each point is set equal to the excess per cubic centimeter of charges on the negative ions over the charges on the positive ions. One obtains (see Appendix A) for the amount of negative electricity $-\sigma_0$ contained in a column of 1 cm^2 cross-section perpendicular to the interface, which equals regarding the absolute value the amount of positive electricity $+\sigma_0$ located in 1 cm^3 of the metal

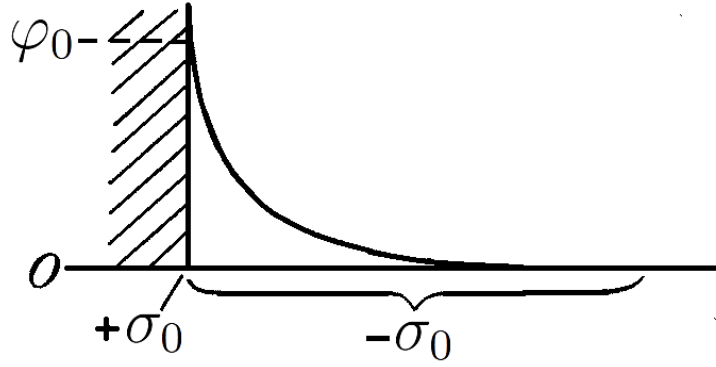


Figure 2: Total potential difference φ_0 and exponential decay of the charge distribution σ_0 in relation to the distance from the metal/solution interface (“amount of negative electricity $-\sigma_0$ ”) towards the interior of the solution at a metal (left)/solution (right) interface

surface, the equation⁶:

$$\sigma_0 = \sqrt{\frac{2\varepsilon_r\varepsilon_0 \mathcal{R} T}{\pi}} \cdot c \cdot \sinh\left(\frac{\mathcal{F} \varphi_0}{2 \mathcal{R} T}\right), \quad (2a)$$

where ε_r is the dielectric constant of water, \mathcal{R} is the universal gas constant, T is the absolute temperature, c is the molar concentration, i.e. the concentration of the salt in mol cm^{-3} , \mathcal{F} is the ionic charge of a gram equivalent, and φ_0 is again the total potential difference between the interior of the solution and the interior of the metal. For the potential curve and charge distribution see Figure 2. The derivation assumes that the concentration of ions directly at the interface remains so small that the gas laws still apply to the osmotic pressure. This means that, for example, for a 1 N solution, the formula can only be used up to potential differences of 0.01 V. This limitation makes its practical usefulness almost illusory. But even in this limited range it is incompatible with the measurements because it gives a capacitance that is far too large (around 263 μF).

It’s easy to see where this discrepancy comes from. The large capacity means that the charges on the negative ions move very close to the positively charged metal surface, and as a simple calculation shows, most of them are much closer than a distance of $1 \times 10^{-8} \text{ cm}$ or 1 \AA . But this is obviously impossible, since

⁶ \mathcal{F} must be converted as follows:

$$\mathcal{F} = e \cdot N_A,$$

where e is in e.s.u. and has the following value: $1.602176634 \times 10^{-19} \cdot 3 \times 10^9 = 4.8065 \times 10^{-10}$ e.s.u.. This gives the value for $\mathcal{F} = \frac{1}{3} \cdot 0.01 \cdot 2.895 \times 10^{14} = 9.649 \times 10^{11}$. Inserting the values for 20 °C results in the argument for the hyperbolic sine as $(19.803 \cdot \varphi_0)$. For example, if $\varphi_0 = 0.02 \text{ V}$ ($1/50 \text{ V}$), the result for $\sinh\left(\frac{\mathcal{F} \varphi_0}{2 \mathcal{R} T}\right)$ is 0.41.

1×10^{-8} cm is the order of magnitude of the ionic radius⁷. In addition, at this distance one can of course no longer calculate with the dielectric constant of water ϵ_r , but rather that of the ions $\tilde{\epsilon}_r$, which also requires a reduction in the capacity. If these circumstances are taken into account, it seems to me that one can easily arrive at the theory described below.

3. Adsorption Theory of the Electrolytic Double Layer

If the temperature were so low that we could neglect the effect of thermal movement, HELMHOLTZ's theory would rightly exist. Any excess negative ions would be located at the interface. If we now increase the temperature, some of them will break away from the interface as a result of the molecular movement due to heat and will be distributed in the solution according to the laws of the diffuse double layer. Accordingly, we idealize the entire Double Layer as follows:

The *positive coverage* is spread over the metal surface with the same density everywhere, the charge is $+\sigma_0$ per cm^2 . The corresponding *negative charge* of the solution also is located partly as a homogeneous surface coverage on a plane parallel to the interface at a distance of δ (average ionic radius); this charge is $-\sigma_1$ per cm^2 , the potential at the point $-\sigma_1$ is φ_1 . The remaining charge is located *diffusely as a continuous spatial charge* in the solution with a density that decreases asymptotically towards the interior of the solution up to zero. $-\sigma_2$ is the entire charge contained in a column with a cross section of 1 cm^2 . The potential φ inside the solution is zero. It is therefore:

$$\sigma_0 = \sigma_1 + \sigma_2 .$$

To clarify the potential curve and the charge distribution, see Figure 3.

Figure 3⁸ also takes into account the experience that, on the one hand, the direct measurements of the double layer capacitance speak for the HELMHOLTZ theory, while on the other hand, the existence of the electrokinetic phenomena shows that part of the negative surface coverage is movable against the interface.

⁷GOUY has already noticed this, but without being able to improve the theory.

⁸As it turned out during a conversation, MESSRS. M. VOLMER and H. CASSEL had also arrived at this picture of the double layer independently of each other.

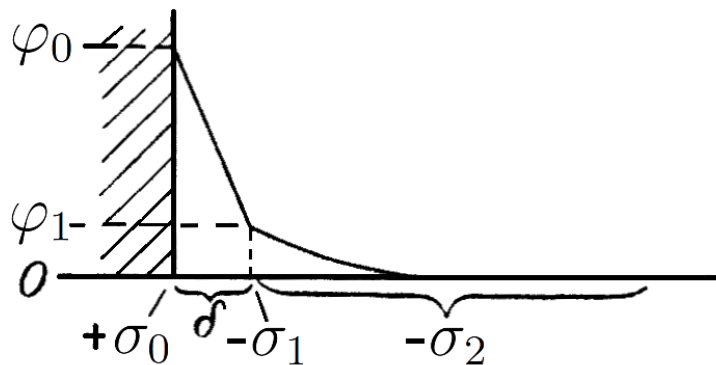


Figure 3: Charge density $+\sigma_0$ (positive surface coverage) at a metal (left)/solution (right) interface and charge density $-\sigma_1$ (negative charge), located on a plane parallel to the former at a distance δ , mean ionic radius. Remaining charge $-\sigma_2$, located diffusely in the solution in the form of a continuous spatial charge with towards the interior of the solution asymptotically decreasing up to zero density

The real problem now is to determine how the negative charge is distributed over these two occupancies, the areal of the molecular capacitor and the spatial of the diffuse double layer, and finally how large σ_1 , φ_1 and also σ_0 are.

We can immediately write down two relationships that correspond to our equations, Equation 1a and Equation 2a, namely:

$$\sigma_0 = \frac{\tilde{\epsilon}_r \epsilon_0}{4\pi\delta} \cdot (\varphi_0 - \varphi_1) , \quad (1)$$

$$\sigma_2 = \sqrt{\frac{2\tilde{\epsilon}_r \epsilon_0 \mathcal{R} T}{\pi}} \cdot \frac{C}{18} \cdot \sinh\left(\frac{\mathcal{F} \varphi_1}{2 \mathcal{R} T}\right) . \quad (2)$$

Here $C = 18 \cdot c$ is the concentration in mole fractions (molecular weight of the water is set equal to 18 g mol^{-1})⁹. We are doing a mistake here by putting the same φ_1 in both equations. Because in Equation 1 φ_1 means the value of the electrical potential prevailing in the first molecular layer of the solution (counted from the interface metal/solution), but in Equation 2 it means that in the second molecular layer. We will see later (page 17) how to correct this error if necessary, but in most cases it is small. However, these two equations do not yet determine φ_1 . On the contrary, we can choose φ_1 arbitrarily, then Equation 1 and Equation 2 give us the corresponding values of σ_0 and σ_2 and thus

$$\sigma_1 = \sigma_0 - \sigma_2 .$$

So there must be a third relationship between these quantities. We get this if

⁹For an example of concentration in mole fraction see Appendix B.

we consider that σ_1 is determined by the forces that keep the ions to stick at the interface. It is if we use $e = \frac{\mathcal{F}}{N_A}$ to denote the charge of a single ion and use z^+ or z^- to denote the number of positive or negative ions adsorbed at the interface per cm^2 ,

$$\sigma_1 = e \cdot (z^- - z^+) .$$

However, according to BOLTZMANN's e theorem, z^+ and z^- are determined by the work

$$W = \epsilon^+ + e \cdot \varphi_1$$

$$W = \epsilon^- - e \cdot \varphi_1$$

that is necessary to bring a positive or negative ion in contact with the interface. Here ϵ^+ or ϵ^- is the usual specific adsorption potential resulting from the molecular forces, which is present for $\varphi_1 = 0$ alone. We ideally assume that ϵ^+ and ϵ^- are different from zero only for the first molecular layer adjacent to the metal surface. The task of calculating the number of ions per cm^2 interface from W is then exactly the same as that solved by the (LANGMUIR) adsorption theory, [7]. We get the solution in the way described below.

We generally consider the adsorption equilibrium that occurs at the interface of a solution. Let W be the work required to bring a molecule of the solute from the interior of the solution into the interface. Furthermore, in equilibrium, let n_1 be the number of adsorbed molecules per cm^2 interface, n_2 the number of dissolved molecules per cm^3 . Let \mathbf{n}_1 and \mathbf{n}_2 , respectively, be the number of dissolved molecules that have just enough room on a maximum of 1 cm^2 interface or in 1 cm^3 solution. We pick out a molecule of the solute and follow it along its path for a long time. It will spend a fraction of t_1 of this time at the interface and a fraction of t_2 in the solution. If W would be zero, i.e. $W = 0$, then $t_1 : t_2$ would simply behave like the numbers of the remaining free spaces in the interface and solution, i.e. it would be

$$\frac{t_1}{t_2} = \frac{\mathbf{n}_1 - n_1}{\mathbf{n}_2 - n_2} .$$

If $W \neq 0$, then this expression has to be multiplied according to BOLTZMANN with the factor $e^{-\frac{W}{k_B T}}$ (k_B is the BOLTZMANN constant). So it turns out that

$$\frac{t_1}{t_2} = \frac{\mathbf{n}_1 - n_1}{\mathbf{n}_2 - n_2} \cdot e^{-\frac{W}{k_B T}} = \frac{n_1}{n_2} ,$$

and since $\frac{t_1}{t_2}$ has the same numerical value for all molecules, this gives, if we do not look at one molecule over a long period of time, but at all molecules at a certain moment:

$$\frac{n_1}{n_2} = \frac{t_1}{t_2} .$$

If the solution is diluted, we can neglect n_2 compared to \mathbf{n}_2 . If we solve the equation for n_1 after replacing $\mathbf{n}_2 - n_2$ by \mathbf{n}_2 , we get:

$$n_1 = \frac{\mathbf{n}_1}{1 + \frac{\mathbf{n}_2}{n_2} \cdot e^{\frac{W}{k_B T}}}.$$

Now $\frac{n_2}{\mathbf{n}_2} \sim C$ is the mole fraction of the solute. The proportionality factor will be of the order of magnitude 1. In the following we set it equal to 1; maintaining it would not significantly change our formulæ. So we replace $\frac{\mathbf{n}_2}{n_2}$ with $\frac{1}{C}$. For a positive or negative ion, $W = \epsilon^+ + e \cdot \varphi_1$ or $W = \epsilon^- - e \cdot \varphi_1$, respectively. This gives us

$$\begin{aligned} z^+ &= \frac{\mathbf{n}_1}{1 + \frac{1}{C} \cdot e^{\frac{\epsilon^+ + e \cdot \varphi_1}{k_B T}}}, \\ z^- &= \frac{\mathbf{n}_1}{1 + \frac{1}{C} \cdot e^{\frac{\epsilon^- - e \cdot \varphi_1}{k_B T}}}, \\ \sigma_1 &= e \cdot (z^- - z^+) \\ &= e \cdot \mathbf{n}_1 \cdot \left(\frac{1}{1 + \frac{1}{C} \cdot e^{\frac{\epsilon^- - e \cdot \varphi_1}{k_B T}}} - \frac{1}{1 + \frac{1}{C} \cdot e^{\frac{\epsilon^+ + e \cdot \varphi_1}{k_B T}}} \right). \end{aligned}$$

Hereby \mathbf{n}_1 is assumed to be the same for both types of ions.

But now there is one point that needs to be discussed in more detail. We acted as if both types of ions were adsorbed independently of each other, i.e. as if the positive ions did not take away any free space on the surface from the negative ones and vice versa. This will be justified if it involves adsorption on a heteropolar substance, such as glass. However, this will not apply to the case of a metal surface. If the same number of positive and negative ions were always adsorbed (which is not possible in reality because then $\sigma_1 = 0$), the 1 in the denominator of the adsorption formula would have to be replaced by 2. A value between 1 and 2 will be correct. Now, if only a few ions are adsorbed, it does not matter whether we set 1 or 2, since both are then negligible compared to the second summand. But if a lot of ions are adsorbed, z^+ and z^- cannot be very different, because otherwise the σ_1 and thus φ_0 would become extremely large. So we won't make a big mistake if we write the value 2 for a metal surface.

Finally, if we introduce instead of molecular values those that are related to 1 mol and denote by Z the number of moles of an ion that can be maximally adsorbed at an interface of 1 cm^2 and by \mathcal{E}^+ or \mathcal{E}^- the adsorption potentials per mole, we

get our third relationship between σ_1 and φ_1 in the form:

$$\sigma_1 = \mathcal{F} \cdot Z \cdot \left(\frac{1}{2 + \frac{1}{C} \cdot e^{\frac{\mathcal{E}^- - \mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} - \frac{1}{2 + \frac{1}{C} \cdot e^{\frac{\mathcal{E}^+ + \mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} \right). \quad (3)$$

If it is the interface of a heteropolar substance, replace the 2 in the denominator with 1. Since this formula or its physical content is actually characteristic of the theory developed here, I would like to call it the adsorption theory of the electrolytic double layer.

If we further add the relationship

$$\sigma_0 = \sigma_1 + \sigma_2, \quad (4)$$

we now have four formulæ, namely Equation 1, Equation 2, Equation 3a and Equation 4 to determine the four unknowns φ_1 , σ_0 , σ_1 and σ_2 .

4. The Capacitance of the Electrolytic Double Layer

4.1. Without Consideration of the Specific Adsorption

We first address the problem of the capacity of the double layer when there is no specific adsorption, i.e. we set $\mathcal{E}^- = \mathcal{E}^+ = 0$. Equation 3 then becomes:

$$\sigma_1 = \mathcal{F} \cdot Z \cdot \left(\frac{1}{2 + \frac{1}{C} \cdot e^{-\frac{\mathcal{F} \cdot \varphi}{\mathcal{R} T}}} - \frac{1}{2 + \frac{1}{C} \cdot e^{\frac{\mathcal{F} \cdot \varphi}{\mathcal{R} T}}} \right). \quad (3a)$$

The following are then considered to be known: φ_0 , the thermodynamically determined potential difference between the interior of the solution and the interior of the metal, and also the capacity of the molecular capacitor $\frac{\tilde{\epsilon}_r \epsilon_0}{4\pi\delta}$ and finally Z . However, the last two quantities are actually only known in terms of their magnitude; their exact value may be found from the appropriate measurements.

To calculate φ_1 , one introduces the values of σ_0 , σ_2 and σ_1 given by Equation 1, Equation 2 and Equation 3a into Equation 4 and thus obtains an equation for φ_1 , which we will call the basic equation, Equation 5a. Inserting the value for φ_1 calculated from this equation into Equation 1 gives σ_0 and thus the total capacity

of the double layer $C = \frac{\sigma_0}{\varphi_0}$. The basic equation is:

$$\left. \begin{aligned} & \underbrace{\frac{\tilde{\varepsilon}_r \varepsilon_0}{4\pi\delta} \cdot (\varphi_0 - \varphi_1)}_{\sigma_0} \\ & = \mathcal{F} \cdot Z \cdot \underbrace{\left(\frac{1}{2 + \frac{1}{C} \cdot e^{-\frac{\mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} - \frac{1}{2 + \frac{1}{C} \cdot e^{\frac{\mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} \right)}_{\sigma_1} \\ & + \underbrace{\sqrt{\frac{2\varepsilon_r \varepsilon_0 \mathcal{R} T}{\pi}} \cdot \frac{C}{18} \cdot \sinh\left(\frac{\mathcal{F} \varphi_1}{2 \mathcal{R} T}\right)}_{\sigma_2} \end{aligned} \right\} \quad (5a)$$

Let us first note the dependence on the concentration C . σ_2 is proportional to \sqrt{C} , while σ_1 is proportional to C at small concentrations. As the concentration decreases, σ_1 will disappear against σ_2 , the diffuse part of the coverage will increasingly predominate over the electrically adsorbed part. At the same time, σ_2 itself will become smaller and smaller, so will $\varphi_0 - \varphi_1$, and the value of φ_1 will get closer and closer to φ_0 . At infinite dilution the theory of the diffuse double layer strictly applies. Conversely, with increasing concentrations – but only up to a certain limit because the adsorption capacity of the adsorbed layer is limited – σ_1 will grow in relation to σ_2 and $\varphi_0 - \varphi_1$ will become larger and larger, i.e. φ_1 getting smaller and smaller. This fact is also the reason why Equation 2 for the diffuse layer here remains applicable up to large values of φ_0 and C , while in section 2 we found that the corresponding Equation 2a is practically worthless because of its limited scope. In order for the laws of dilute solutions used in their derivation to remain valid, the concentration of an ion at any point must not exceed the order of magnitude $1 \times 10^{-3} \text{ mol cm}^{-3}$. Now the maximum value of the concentration of an ion in section 2 is $c \cdot e^{\pm \frac{\mathcal{F} \varphi_0}{\mathcal{R} T}}$, whereas here it is $\frac{C}{18} \cdot e^{\pm \frac{\mathcal{F} \varphi_1}{\mathcal{R} T}}$ (where $c = \frac{C}{18}$ is the concentration inside the solution). But as we have just seen, for large values of C the value of φ_1 is very small and only for very small C values φ_1 is large, so that for the normally occurring φ_0 -values of the order of 1 V our Equation 2 remains applicable from very small concentrations up to those of over 1 mol L^{-1} and only at higher concentrations should be replaced by Equation 7 in the appendix.

When using the basic formula for numerical calculations, it is more convenient not to calculate the value of φ_1 associated with a specific value of φ_0 , but vice versa to start from a specific value of φ_1 or $\frac{\mathcal{F} \varphi_1}{\mathcal{R} T}$, respectively, and calculate the corresponding value of φ_0 . In addition, the basic formula can often be greatly simplified through suitable approximate calculations. So for small values of C and φ_1 in the equation for σ_1 one can neglect the 2 in the denominator – which physically means that the mutual taking away of positions of the electrically adsorbed ions is

not taken into account. We then have

$$\sigma_1 = \mathcal{F} \cdot Z \cdot C \cdot \left(e^{\frac{\mathcal{F} \varphi_1}{\mathcal{R} T}} - e^{-\frac{\mathcal{F} \varphi_1}{\mathcal{R} T}} \right)$$

or

$$\sigma_1 = 2 \mathcal{F} \cdot Z \cdot C \cdot \sinh \left(\frac{\mathcal{F} \varphi_1}{\mathcal{R} T} \right),$$

respectively. E.g. for a 0.5 N solution and $\varphi_1 = 0.25$ V ($1/4$ V) C is equal to 9×10^{-3} and $\frac{\mathcal{F} \varphi_1}{\mathcal{R} T} = 0.99 \cong 1$; In this case, the error of the simplified formula is 5 %. Furthermore, if φ_1 is so small (below 0.01 V), and therefore $\frac{\mathcal{F} \varphi_1}{\mathcal{R} T}$ is small compared to 1, then one can expand the e -function in a series and stop with the first term. Then the basic formula takes the form:

$$\frac{\tilde{\varepsilon}_r \varepsilon_0}{4\pi\delta} \cdot (\varphi_0 - \varphi_1) = \left(2 \mathcal{F} Z C + \sqrt{\frac{\varepsilon_r \varepsilon_0 \mathcal{R} T}{2\pi} \cdot \frac{C}{18}} \right) \cdot \frac{\mathcal{F} \varphi_1}{\mathcal{R} T}.$$

So this equation is a simple linear equation in φ_1 .

To give an overview of the expected values of φ_1 and $C = \frac{\sigma_0}{\varphi_0}$, some numerical examples are given. For this purpose we have to assume certain numerical values for $C_0 = \frac{\tilde{\varepsilon}_r \varepsilon_0}{4\pi\delta}$ and Z . We know the value of C_0 for the electrode Hg/1 N-KNO₃, aq quite precisely from the measurements by KRÜGER and KRUMREICH, [6]. They find that the electrocapillary curve in this case is pretty much a parabola. This means that the capacity C of the double layer is independent of the potential φ_0 . So here $C = C_0$, which is also to be expected according to our theory, as the following calculations show. KRÜGER gives the value $27 \mu\text{F} = 2.43 \times 10^7 \text{ cm}$ for C_0 . We will see that with a 1 N solution the found value of C is even 5 % to 6 % smaller, i.e. C_0 , and set approximately $C_0 = 2.6 \times 10^7 \text{ cm}$. We can only estimate the value of Z by order of magnitude, but fortunately, as we will see below, a power of ten is not important here. We set Z equal to the number of moles of water contained in the side surface of a 1 cm cube, i.e. $Z = 1.724 \times 10^{-9} \text{ mol cm}^{-2}$ ¹⁰. With these values our simplified basic equation becomes:

$$\begin{aligned} & 2.5 \times 10^7 \cdot (\varphi_0 - \varphi_1) \\ &= \left(9.82 \times 10^5 \cdot C + 1.322 \times 10^5 \cdot \sqrt{C} \right) \cdot 1.188 \times 10^4 \cdot \varphi_1 \end{aligned}$$

or:

$$\frac{\varphi_0}{\varphi_1} = 1 + 4.66 \times 10^2 \cdot C + 0.624 \times 10^2 \cdot \sqrt{C}.$$

¹⁰ $Z = \frac{\left(\frac{6.022 \cdot 14 \times 10^{23}}{18} \right)^{\frac{2}{3}}}{6.022 \cdot 14 \times 10^{23}}$

φ_1	φ_0	$100 \cdot \frac{\varphi_1}{\varphi_0}, \%$	$\frac{\sigma_1}{\sigma_0}$	Conc.
very small	very small	6.4	1.07	1 N
0.05	1.06	4.5	1.22	
very small	very small	56	0.108	0.01 N
0.1	0.302	33	0.37	
0.15	0.914	16.4	0.87	

Table 2

φ_1	$\bar{\varphi}_0$	$100 \cdot \frac{\bar{\varphi}_1}{\bar{\varphi}_0}, \%$	$\frac{\sigma_1}{\sigma_2}$	Conc.
very small	very small	12.4	0	1 N
0.08	1.05	7.7	0	
very small	very small	59	0	0.01 N
0.11	0.291	38	0	
0.18	0.924	19.5	0	

Table 3

From matching values of φ_1 and φ_0 we easily get $C = \frac{\sigma_0}{\varphi_0}$. Because it is

$$C_0 \cdot (\varphi_0 - \varphi_1) = \sigma_0,$$

therefore

$$C = \frac{\sigma_0}{\varphi_0} = C_0 \cdot \left(1 - \frac{\varphi_1}{\varphi_0}\right).$$

So C is $100 \cdot \frac{\varphi_1}{\varphi_0} \%$ smaller than C_0 . Table 2 is calculated with the above values of C_0 and Z for a 1 N and a 0.01 N solution.

In the 1 N solution, as claimed above, C is almost constant (from $\varphi_0 = 0$ to $\varphi_0 = 1$ V) and around 6.4 % to 4.5 % smaller than C_0 . In contrast, for the 0.01 N solution, C already varies considerably with φ_0 and is not yet half as large as C_0 for small potential differences. The electrocapillary curve will therefore be more flattened and will no longer be a parabola. The last column indicates how much of the negative charge contained in the liquid is bound in form of coverage to the molecular capacitor and how much is diffusely distributed. $\frac{\sigma_1}{\sigma_2} = 1$ means that both parts are equal. In the 1 N solution the first part predominates somewhat, in the 0.01 N solution the diffuse part predominates, but one can see how the latter recedes more and more as the potential difference increases.

For the case just discussed (pure electrical adsorption, $\mathcal{E}^- = \mathcal{E}^+ = 0$) we now have the possibility of estimating the above-mentioned error that we made by setting the electrical potential in the first and second molecular layer equal, i.e. to have introduced the same value of φ_1 in Equation 2 as in Equation 1 and Equation 3. We can idealize this case more easily and without this error by counting the first molecular layer as part of the diffuse layer, i.e. setting $\sigma_1 = 0$. Table 3 gives the values calculated under this assumption. The deviations from Table 2 are not large. This also proves our claim that the exact value of Z is not important, because from $Z = 0$ also follows $\sigma_1 = 0$ and the values of Table 3. Finally, it would not be difficult to eliminate the above error by introducing the value φ_2 of the potential in the second molecular layer instead of φ_1 in Equation 2 for the diffuse layer and to supplement our system of equations by another equation

$$\sigma_2 = C' \cdot (\varphi_1 - \varphi_2) ,$$

where C' is the capacitance of the capacitor between the first and second molecular layers. However, since the error is not very significant, this has initially been ignored in order to simplify matters as much as possible.

It may seem as a rather paradoxical result that, for example, with a 1 N solution at a potential difference of 1 V, the capacity of the double layer only decreases by 7.7% than that of the pure molecular double layer, although the total negative charge is diffusely distributed. However, the result is immediately understandable from a physical point of view if one considers (i) that the diffuse layer only begins at a distance δ (average ionic radius) from the interface and (ii) the density drop in the former is very steep at high concentrations and potential differences, so that the entire negative charge is densely packed near the plane where it is located at the molecular capacitor.

4.2. With Consideration of the Specific Adsorption

Our basic equation, if \mathcal{E}^- and \mathcal{E}^+ are not set to zero, is as follows:

$$\left. \begin{aligned} & \underbrace{C_0 \cdot (\varphi_0 - \varphi_1)}_{\sigma_0} \\ & = \mathcal{F} \cdot Z \cdot \underbrace{\left(\frac{1}{2 + \frac{1}{C} \cdot e^{\frac{\mathcal{E}^- - \mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} - \frac{1}{2 + \frac{1}{C} \cdot e^{\frac{\mathcal{E}^+ + \mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} \right)}_{\sigma_1} \\ & + \underbrace{\sqrt{\frac{2\varepsilon_r \varepsilon \mathcal{R} T}{\pi}} \cdot \frac{C}{18} \cdot \sinh \left(\frac{\mathcal{F} \varphi_1}{2 \mathcal{R} T} \right)}_{\sigma_2} \end{aligned} \right\} \quad (5)$$

We now want to draw some conclusions for the shape of the electrocapillary curve from this theory, supplemented by taking specific adsorption into account.

If initially $\mathcal{E}_1 = \mathcal{E}_2$, the electrocapillary curve remains symmetrical, and its maximum ($\sigma_0 = 0$) is at the absolute zero point of the potential ($\varphi_0 = 0$) footnote. On the other hand, the value of the maximum surface tension, i.e. the height of the electrocapillary curve, will of course depend on the adsorbability of the salt.. If $\mathcal{E}_1 = \mathcal{E}_2$ is positive, i.e. the ions are driven out of the interface by the specific adsorption forces, then compared to the case discussed in section 3, where $\mathcal{E}^+ = \mathcal{E}^- = 0$ the value of σ_1 and thus the capacity itself is reduced. If $\mathcal{E}_1 = \mathcal{E}_2$ is negative, i.e. the ions are accumulated in the interface, then conversely σ_1 will be larger than in section 3 and values for the capacitance show smaller deviations from the maximum value C_0 than in section 3.

If $\mathcal{E}^+ \neq \mathcal{E}^-$, i.e. the ions are adsorbed to different degrees, the electrocapillary curve becomes asymmetrical. The maximum ($\sigma_0 = 0$) does not correspond to the absolute zero point of the potential ($\varphi_0 = 0$), but the relationships

$$\varphi_0 = \varphi_1, \quad \sigma_1 = -\sigma_2$$

apply to the maximum ($\sigma_0 = 0$) because of

$$C_0 \cdot (\varphi_0 - \varphi_1) = \sigma_0 = \sigma_1 + \sigma_2 = 0.$$

The potential drop in the molecular capacitor is zero, the entire potential difference $\bar{\varphi}_0$ is located in the diffuse layer. The charge of the positive occupancy of the molecular capacitor is zero, the charge of the negative one is inversely equal to the charge contained in the diffuse layer (see Figure 4). From the course of the electrocapillary curve one should be able to calculate \mathcal{E}^+ and \mathcal{E}^- . However, since the difference in the ionic radius δ and, above all, the dielectric constant ε_r of the positive and negative ions also plays an important role in the asymmetry of the curve, while in this case δ and ε_r would be set equal for both ions, this topic will be discussed in a later publication. It should only be briefly noted that GOUY (l.c.) observed the effect that the capacity is in general constantly decreasing from the positive branch of the electrocapillary curve, where more negative ions are adsorbed, towards the negative branch, where more positive ions are adsorbed. This apparently is due to the fact that the electrons in the negatively charged ions are easier to move than in the positively charged ones and thus the decrease in capacity is caused by the decrease in ε_r .

Finally, it should be noted that if the two types of ions are adsorbed to very different extents, it can easily happen that φ_0 and φ_1 have different signs (see Figure 5).

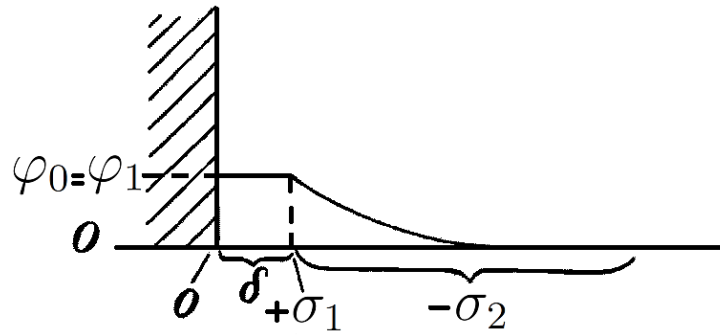


Figure 4: Potential curve and charge distribution in the molecular capacitor

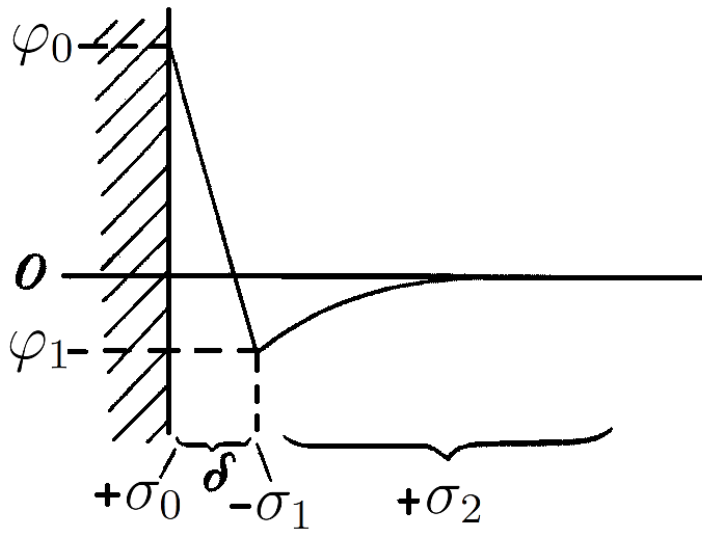


Figure 5: Different signs of potential difference φ in case of different adsorption intensity of both ion types

5. Electrokinetic Potential (ζ -Potential of Freundlich)

If the solution moves relative to the interface, the molecular layers directly adjacent to the interface will adhere to it and will not follow the movement of the solution. The value of the potential on the plane that separates the moving from the fixed layers is the electrokinetic ζ -potential¹¹. Since at least the first molecular layer adjacent to the interface adheres to it, φ_1 is at least as large as ζ . It is possible that φ_1 is larger than ζ , namely if several layers are fixed. Now the electrokinetic phenomena always involve extremely dilute solutions (micromoles to millimoles per liter), in which φ does not change very much over a distance of 1×10^{-8} cm. In this case, we will not make a serious mistake if we simply identify the ζ -potential with φ_1 , which should always hold good in the following.

Our basic equation then gives us the absolute value φ_1 for *all* (not too high) concentrations. If C is infinitely small, then here too $\sigma_1 = 0$, $\sigma_2 = 0$ and $\varphi_1 = \varphi_0$. However, such high dilutions are practically impossible to achieve. In reality, most measurements are carried out at concentrations where $\sigma_2 \ll \sigma_1$, i.e. the charge of the solution is mostly located in the adsorption layer. If we can neglect σ_2 next to σ_1 , we have the equation for φ_1 :

$$C_0 \cdot (\varphi_0 - \varphi_1) = \mathcal{F} \cdot Z \cdot \left(\frac{1}{1 + \frac{1}{C} \cdot e^{\frac{\mathcal{E}^- - \mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} - \frac{1}{1 + \frac{1}{C} \cdot e^{\frac{\mathcal{E}^+ + \mathcal{F} \cdot \varphi_1}{\mathcal{R} T}}} \right).$$

This equation is quadratic in C , so the curve will show a maximum or minimum for φ_1 plotted as a function of C . This has actually been observed in many cases. Solving the equation for C gives the value of the concentration at which φ_1 is an extremum:

$$C_m = e^{\frac{\mathcal{E}_1 + \mathcal{E}_2}{2 \mathcal{R} T}} = e^{-\frac{Q}{2 \mathcal{R} T}},$$

if we use Q to denote the heat of adsorption of one mole of salt. Direct measurements of Q would therefore allow a good test of the theory. But also the extremal value of φ_1 has a simple physical meaning. If $\mathcal{F} \cdot \varphi_1$ took the value $\frac{1}{2} \cdot (\mathcal{E}^- - \mathcal{E}^+)$, the right side of the equation would become zero because

$$\mathcal{E}^- - \mathcal{F} \cdot \varphi_1 = \mathcal{E}^+ + \mathcal{F} \cdot \varphi_1 = \frac{1}{2} \cdot (\mathcal{E}^- - \mathcal{E}^+) = \mathcal{F} \cdot \bar{\varphi}_1$$

and as a result the charge per unit area would become $\sigma_0 = \sigma_1 = 0$. So φ_1 cannot take the value $\bar{\varphi}_1$. On the other hand, if $|\mathcal{E}^- - \mathcal{E}^+|$ is large, φ_1 cannot be very different from $\bar{\varphi}_1$, because otherwise the value of the charge would become too large, as rough numerical calculations show. So, just to make the equation more

¹¹For a detailed explanation see https://en.wikipedia.org/wiki/Zeta_potential

symmetrical, it makes sense to set $\varphi_1 = \bar{\varphi}_1 + \varphi'_1$. Let's do this and further assume that $\frac{\mathcal{F}\varphi'_1}{\mathcal{R}T} \ll 1$, so that we can expand the power of $e\varphi$ and terminate with the linear term. After a simple transformation, our equation then takes the form:

$$\varphi'_1 = \left(2 + \frac{C}{C_m} + \frac{C_m}{C}\right) \cdot \frac{\mathcal{R}TC_0}{2Z_0\mathcal{F}^2} \cdot (\varphi_0 - \varphi_1) .$$

With the numerical values used above we have

$$\frac{\mathcal{R}TC_0}{2Z_0\mathcal{F}^2} = 2.050 \times 10^{-3} = C .$$

Further, at the extremal value $C = C_m$ holds, therefore

$$\varphi'_1 = 4 \cdot 2.050 \times 10^{-3} \cdot (\varphi_0 - \varphi_1) = 8.20 \times 10^{-3} \cdot (\varphi_0 - \varphi_1) .$$

Since $(\varphi_0 - \varphi_1)$ is at most about 1 V, at the maximum φ'_1 is at most a few millivolts, i.e. $\varphi_1 = \bar{\varphi}_1 + \varphi'_1$ is almost $\bar{\varphi}_1$. This gives us the opportunity to calculate the adsorption potentials \mathcal{E}^+ and \mathcal{E}^- individually from the values of the concentration and the ζ -potential at the maximum using the following formulæ:

$$\begin{aligned} \mathcal{E}^- + \mathcal{E}^+ &= 2\mathcal{R}T \cdot \ln(C_m) \\ \mathcal{E}^- - \mathcal{E}^+ &= 2\mathcal{F}(\varphi_1)_m \sim 2\mathcal{F}\bar{\varphi}_1 . \end{aligned}$$

The values measured on glass capillaries with different salts are in the range of a few tenths of millimoles per liter for C_m (i.e. for C_m a value of a few 1×10^{-6}) and around a few hundredths of a volt for $\bar{\varphi}_1$. This results in adsorption potentials of 10,000 to 15,000 cal per equivalent.

Whether the ζ - C curve has a maximum or a minimum depends on the sign of $(\varphi_0 - \bar{\varphi}_1)$. Because at the extremum

$$\frac{d^2\varphi_1}{dC^2} = (\varphi_0 - \bar{\varphi}_1) \cdot \frac{2 \cdot C}{\left(\frac{C}{C_m}\right)^3} \cdot \frac{1}{1 + 4 \cdot C} ,$$

applies, where again $\bar{\varphi}_1$ is set for $(\varphi_1)_m$. For example, if φ_0 is negative, as with glass, then if $|\bar{\varphi}_2| < |\varphi_0|$, $(\varphi_0 - \bar{\varphi}_2)$ and $\frac{d^2\varphi_2}{dC^2}$ are also negative and the ζ - C curve has a maximum. Only when $|\bar{\varphi}_1| > |\varphi_0|$ and $\bar{\varphi}_1$ is also negative, i.e. the negative ions are adsorbed much more strongly than the positive ones, $(\varphi_0 - \varphi_1)$ becomes positive and the ζ - C curve shows a minimum.

It should be particularly pointed out that the signs of the thermodynamic potential φ_0 and the ζ potential φ_1 are independent of each other, which has already been emphasized by FREUNDLICH and was also qualitatively pointed out by him

in a similar way as above.

To calculate the curve shape at a greater distance from the maximum, one of course has to use the basic equation and then in general σ_2 can be neglected no longer anymore.

6. Summary

An attempt has been made above to gain clarity about the constitution of the electrolytic double layer. It was assumed that the double layer can be ideally replaced by a capacitor, whose coverage on the surface of the solid substance is formed by a surface-wide and homogeneously distributed charge, while the other coverage located in the solution is formed by a homogeneous surface-wide charge that is immediately followed by a spatial charge with a density that decreases towards the interior of the solution. Based on this picture, Equation 5 was derived, which is intended to summarize the theories of polarization capacity, the electrocapillary curve and the electrokinetic potential. It is obvious that this goal could only be achieved through strong idealization and simplification. Only a binary monovalent salt was considered. The radius δ , the dielectric constant $\tilde{\epsilon}_r$ and the number n_1 of available sites per cm^2 interface for both ion types were set equal. Also the electrical potential φ_1 in the first and second molecular layers was set equal, and it was assumed that the specific adsorption forces only extend over one molecular layer. Further, what was not particularly emphasized, it was assumed that the adsorption potential \mathcal{E} is independent of the number of adsorbed ions. On the one hand, it seems to me that it will now be easy to take all of these neglects into account on the way proceeded here and to improve and generalize the theory. And on the other hand, it seems to me that the theory, even in its current primitive form, correctly reflects the previously known complex of facts in a broad sense. Above all, the theory gives account of the facts

1. that the polarization capacitance is almost equal to the capacitance of the molecular capacitor, although the majority of the solution's charge is diffusely distributed,
2. that the electrokinetic potential is much smaller than the NERNST thermodynamic potential and can even have the opposite sign, and
3. to oversee in an approximately quantitatively manner the dependence of the shape of the electrocapillary curve and the electrokinetic potential on the concentration of the salt and the adsorption potentials of the two ions, and conversely to calculate the approximate value of the adsorption potentials from the measurements.

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A. Calculating the Basic Equation of Equation 2a

Equation 2a may be derived in short by the following procedure:

In the metal-solution interface, which is assumed to be flat, we place the x - y plane of a Cartesian coordinate system whose positive z axis points into the solution. The potential φ and the density ρ of the positive electricity then depend only on the z coordinate. Both quantities are connected by the equation:

$$\Delta\varphi = \frac{d^2\varphi}{dz^2} = -\frac{4\pi}{\varepsilon_r\varepsilon_0} \cdot \rho. \quad (6)$$

For $z = \infty$ it follows that $\varphi = 0$, $\frac{d\varphi}{dz} = 0$, $\rho = 0$, for $z = 0$ it follows that $\varphi = \varphi_0$, $\frac{d\varphi}{dz} = -\frac{4\pi}{\varepsilon_r\varepsilon_0} \cdot \sigma_0$, if σ_0 is again the surface density of electricity at the metal-solution interface. (The same equation can be obtained if one calculates the amount of electricity

$$-\sigma_0 = \int_0^\infty \rho dz$$

contained in a column parallel to the z axis with a cross-section of 1 using Equation 6.)

To get $\frac{d\varphi}{dz}$, we multiply Equation 6 on both sides by $\frac{d\varphi}{dz} dz$ and integrate from $z = 0$ to $z = \infty$. This results in:

$$\begin{aligned} \frac{1}{2} \cdot \left(\frac{d\varphi}{dz} \right)^2 \Big|_0^\infty &= -\frac{4\pi}{\varepsilon_r\varepsilon_0} \cdot \int_{\varphi_0}^0 \rho d\varphi, \\ \left(\frac{d\varphi}{dz} \right)_0 &= \sqrt{\frac{8\pi}{\varepsilon_r\varepsilon_0} \cdot \int_{\varphi_0}^0 \rho d\varphi}. \end{aligned}$$

Therefore:

$$\sigma_0 = -\frac{\varepsilon_r\varepsilon_0}{4\pi} \cdot \left(\frac{d\varphi}{dz} \right)_0 = -\sqrt{\frac{\varepsilon_r\varepsilon_0}{2\pi} \cdot \int_{\varphi_0}^0 \rho d\varphi}.$$

If we use c^+ or c^- to denote the concentration of the positive or negative ions in moles per unit volume, then for $z = \infty$: $c^+ = c^- = c^\infty$, and thus for any z according to BOLTZMANN:

$$\begin{aligned} c^+ &= c^\infty \cdot e^{-\frac{\mathcal{F}\varphi}{\mathcal{R}T}}, \\ c^- &= c^\infty \cdot e^{+\frac{\mathcal{F}\varphi}{\mathcal{R}T}}, \\ \rho &= \mathcal{F} \cdot (c^+ - c^-) = \mathcal{F} \cdot c^\infty \cdot \left(e^{-\frac{\mathcal{F}\varphi}{\mathcal{R}T}} - e^{\frac{\mathcal{F}\varphi}{\mathcal{R}T}} \right). \end{aligned}$$

Inserted into the above expression for σ_0 and integration yields, after a simple transformation, Equation 2a.

As one can see, $\int \rho d\varphi$ is only easy to evaluate if ρ is a function of φ alone and does not explicitly depend on z . This is probably the reason why it has not yet been possible to take the specific adsorption of ions into account in the theory, while the theory outlined above avoids this difficulty through idealizing assumptions.

On the other hand, it is easy to introduce the laws of ideal concentrated solutions (colored molecules!) instead of the gas laws for osmotic pressure. Under this assumption it follows

$$\sigma_0 = \sqrt{\frac{\varepsilon_r \varepsilon_0 \mathcal{R} T}{2\pi 18}} \cdot \sqrt{\ln \left[1 + \frac{4C}{(1+C)^2} \cdot \sinh^2 \left(\frac{\mathcal{F} \varphi_0}{2 \mathcal{R} T} \right) \right]}, \quad (7)$$

which is transformed into Equation 2a as follows:

Equation 7 has the form

$$\sigma_0 = \sqrt{\frac{\varepsilon_r \varepsilon_0 \mathcal{R} T}{2\pi 18}} \cdot \sqrt{\ln(1+x)}.$$

If we now expand the $\ln(1+x)$ in a TAYLOR series around $x_0 = 0$ in the case of $|x|$ being < 1 we get

$$\ln(1+x) \cong x - \frac{x^2}{2} + \dots$$

If we only consider the first term of the series then we have

$$\sigma_0 = \sqrt{\frac{\varepsilon_r \varepsilon_0 \mathcal{R} T}{2\pi 18}} \cdot \sqrt{\frac{4C}{(1+C)^2} \cdot \sinh^2 \left(\frac{\mathcal{F} \varphi_0}{2 \mathcal{R} T} \right)}.$$

This may be written as

$$\sigma_0 = \sqrt{\frac{\varepsilon_r \varepsilon_0 \mathcal{R} T}{2\pi}} \cdot \sqrt{\frac{C}{18}} \cdot \frac{2}{(1+C)} \cdot \sinh \left(\frac{\mathcal{F} \varphi_0}{2 \mathcal{R} T} \right).$$

$\frac{1}{(1+C)} \approx 1$, because $0 \leq C \leq 1$ and so may be disregarded, which gives, bearing in mind that $c = \frac{C}{18}$ (see page 12),

$$\sigma_0 = \sqrt{\frac{2\varepsilon_r \varepsilon_0 \mathcal{R} T}{\pi}} \cdot \sqrt{c} \cdot \sinh \left(\frac{\mathcal{F} \varphi_0}{2 \mathcal{R} T} \right),$$

which is identical to Equation 2a.

B. Concentration in Mole Fraction, Exemplary Calculation

Here, an exemplary calculation regarding the *concentration in mole fraction* of a binary solution is given according to <https://homework.study.com/explanation/what-is-the-concentration-in-mole-fraction-of-solute-of-a-1-05m-aqueous-solution-of-potassium-nitrate-kno3-the-density-of-the-solution-is-1-06-g-ml.html>

Question:

What is the concentration in mole fraction of solute of a 1.05 M aqueous solution of potassium nitrate, KNO_3 ? The density of the solution is 1.06 g mL^{-1} .

The Concentration of Solutions:

There are different ways of expressing the concentrations of solutions, specifically indicating the amount of solute in the solution. These expressions of solutions are molarity c , molality, mole fraction C , mass percent, etc.

Answer and Explanation:

Given initial conditions:

We assume a 1-liter volume of the solution,

molarity of solution, $c = \frac{n}{V}$, $c = 1.05 \text{ M} = \frac{1.05 \text{ mol solute}}{\text{L solution}}$

density of solution, $\rho = 1.06 \text{ g mL}^{-1}$

volume of solution, $V = 1.0 \text{ L}$

molecular weight of KNO_3 , $\mathcal{M}_{\text{KNO}_3} = 101.1 \text{ g mol}^{-1}$

molecular weight of water, H_2O , $\mathcal{M}_{\text{H}_2\text{O}} = 18 \text{ g mol}^{-1}$

Solving for the mass of the solution, m_{sol} , using the density equation according to:

$$\rho = \frac{m_{\text{sol}}}{V}$$

and rearranging to solve for the mass, we obtain

$$\begin{aligned} m_{\text{sol}} &= \rho \cdot V = 1.06 \text{ g mL}^{-1} \cdot \frac{1000 \text{ mL}}{1 \text{ L}} \cdot 1 \text{ L} \\ &= 1060 \text{ g}. \end{aligned}$$

From the given molarity and volume of solution, we have 1.05 moles of KNO_3 , n_{KNO_3} .

Solving for the mass of KNO_3 , m_{KNO_3} ,

$$\begin{aligned} m_{\text{KNO}_3} &= n_{\text{KNO}_3} \cdot \mathcal{M}_{\text{KNO}_3} = 1.05 \text{ mol} \cdot 101 \text{ g mol}^{-1} \\ &= 106.155 \text{ g} \end{aligned}$$

Solving for the mass of water, $m_{\text{H}_2\text{O}}$,

$$\begin{aligned} m_{\text{sol}} &= m_{\text{KNO}_3} + m_{\text{H}_2\text{O}} \\ 1060 &= 106.155 + m_{\text{H}_2\text{O}} \\ m_{\text{H}_2\text{O}} &= 1060 - 106.155 \\ m_{\text{H}_2\text{O}} &= 953.845 \text{ g}. \end{aligned}$$

The moles of water, $n_{\text{H}_2\text{O}}$, for calculating the mole fraction, is determined according to

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{\mathcal{M}_{\text{H}_2\text{O}}} = \frac{953.845 \text{ g}}{18 \text{ g mol}^{-1}} = 52.9914 \text{ mol}.$$

The mole fraction of the KNO_3 is

$$\text{mole fraction } \text{KNO}_3 = \frac{n_{\text{KNO}_3}}{n_{\text{KNO}_3} + n_{\text{H}_2\text{O}}} = \frac{1.05}{1.05 + 52.9914}$$

which finally yields for the concentration C in mole fraction:

$$\text{mole fraction } \text{KNO}_3 = 0.0194$$

C. Calculations regarding Capacitance with actual Constants

We have seen on page 8 that the experimentally determined capacitance C per cm^2 of the double layer capacitor on a mercury electrode is $24 \mu\text{F}$. This value may also be calculated, where from now on actual values of the constants are used in the following calculations, which may be found at the relevant sources in the internet.

The capacitance mentioned above is calculated by starting with the formula by DEBYE and HÜCKEL, [2], which reads

$$\frac{1}{\varkappa} = \frac{3.043}{\sqrt{\gamma}} \cdot 1 \times 10^{-8} \text{ cm}, \quad (8)$$

if for the relative permittivity (or dielectric constant) of water at 20 °C the value 80.0 is used. For $\gamma = 1 \text{ mol L}^{-1}$ the characteristic length to be used is then $3.0430 \times 10^{-8} \text{ cm}$ or 3 \AA . The Capacitance is

$$C = \frac{\varepsilon_r \varepsilon_0}{4\pi\delta},$$

where δ is the mean ionic radius or diameter, respectively, and may correspond to $\frac{1}{\varkappa}$. If the value for $\frac{1}{\varkappa}$ is inserted into the above equation according to

$$C = \frac{\varepsilon_r \cdot \varepsilon_0}{4\pi \cdot \varkappa^{-1}} \cdot 1 \times 10^6,$$

a capacitance of approximately 19 μF results. The quotient $\frac{\delta}{\varepsilon_r \varepsilon_0} \sim 0.42 \times 10^{-8} \text{ cm}$ or 0.4 \AA .

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